



A Review of Laser Photofragmentation/Fragment Detection Techniques for Chemical Analysis of the Gas Phase

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A Review of Laser Photofragmentation/Fragment Detection Techniques for Chemical Analysis of the Gas Phase

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Abstract

Laser photofragmentation/fragment detection techniques utilize one or multiple lasers for photolysis of the analyte species and spectroscopic detection of the characteristic photofragments. Fragment detection techniques include laser-induced fluorescence, photoionization, prompt emission, stimulated emission, and laser ionization recombination emission spectroscopies. Applications for chemical analysis of the gas phase have been performed by the detection of atomic and molecular fragments. Recent reports on photofragmentation/fragment detection approaches are presented, and the outlook for future applications is discussed.

Acknowledgments

We thank our numerous colleagues who provided us with reprints/preprints of their work. R. C. Sausa also thanks Dr. V. Swayanbunathan for helpful discussions. J. B. Simeonsson gratefully acknowledges support from the University of Iowa through the Old Gold Fellowship program.

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1. Introduction

Laser-based spectrometric techniques are useful for chemical analysis because they offer the combination of high sensitivity and selectivity with real-time monitoring capabilities. There continues to be interest in the development of laser-based photofragmentation/fragment detection (PF/FD) techniques for gaseous analytes due to the fact that laser technology is rapidly maturing and is often capable of being implemented outside of the research laboratory. Also, there is a constant need for ever higher levels of analytical performance in terms of sensitivity, selectivity, and temporal response. The purpose of this article is to review the status of spectrochemical techniques based on PF/FD methods. The PF/FD approach is first discussed in terms of its analytical utility and the strategies that can be implemented for fragment detection. Early reports viewed as important to the development of current techniques are noted, as are previous reviews of this field of PF/FD research. Presented are recent applications of PF/FD techniques for chemical analysis that include the detection of analytes by characteristic atomic fragments or molecular fragments. Finally, the results of the review are summarized and areas of future applications are identified. A glossary of useful abbreviations and terms is also included at the end of the review.

2. PF/FD Approach

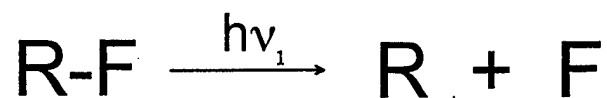
The PF/FD approach is most often utilized when the analyte molecule does not lend itself to direct spectroscopic detection. In general, atoms and small molecules (e.g., diatomic and triatomic species) can be detected directly by absorption, fluorescence, or photoionization spectroscopy techniques due to a favorable combination of usually strong optical transitions and sharp, well-resolved spectral features. However, it is often the case for larger molecules that the transitions are weaker and the spectral features are broad and poorly defined, in which case direct detection of the molecule by the above methods is not analytically practical. While direct detection may not be feasible, the photofragmentation products of polyatomic molecules are often monatomic and diatomic species that are readily detected. Since the fragments are characteristic of the chemical composition of the precursor (analyte), they also contribute to the selectivity of the method. It is

important to note that the PF process has a spectral dependence which can be exploited to increase the selectivity of PF/FD approaches. One important feature of the PF/FD method is its utility for the detection of classes of compounds. When molecules share a common functionality (e.g., -Cl, -Br, -I, -NO₂, -SO₂/-SO₄), the functionality may be targeted for fragmentation and detection. Optimization of the technique for the detection of a characteristic fragment allows a class of compounds to be detected by a single spectroscopic approach.

A schematic diagram showing the basis of the PF/FD method is presented in Figure 1. The analyte or precursor molecule, R-F, is initially excited by a single or multiphoton absorption process using laser radiation, $h\nu_1$, resonant with an absorption feature of the analyte molecule. Following excitation, fragmentation occurs and yields the characteristic fragment, F, with internal energy, $E(j,v,e)$, and its companion radical, R. The letters j, v, and e denote the fragment's internal energy due to rotational, vibrational, and electronic excitation. A second laser source, $h\nu_2$, which may be time-delayed from the first, can then be used to probe the fragment distribution by laser-induced fluorescence (LIF), photoionization (PI), laser ionization recombination emission (LIRE), or stimulated emission (SE). In some cases, the photofragment population may be produced with sufficient electronic excitation so that it either emits spontaneously or absorbs additional photons, resulting in prompt photoionization (PPI). The former process is sometimes referred to as prompt emission (PE) or fragment fluorescence (FF) and should be distinguished from LIF following the photofragmentation process. A special case of the PF/FD method occurs when the condition $h\nu_1 = h\nu_2$ is satisfied. In this case, one laser can be used for both photofragmentation of the precursor molecules and excitation of the characteristic fragments.

Spectrochemical measurements using each of the above-mentioned detection techniques have been reported. The relative effectiveness of each approach depends on the analyte (precursor) and fragment species in question. Due to the high laser intensity required for the photofragmentation process, the photoproduction of interferences is a key consideration in selecting the optimum method of fragment detection. Although PF/LIF has seen the widest application and perhaps the highest degree of success, it should be pointed out that the combination of laser photofragmentation followed by PI detection of the fragment with mass spectrometric detection has perhaps the

1. Photofragmentation



2. Fragment Detection

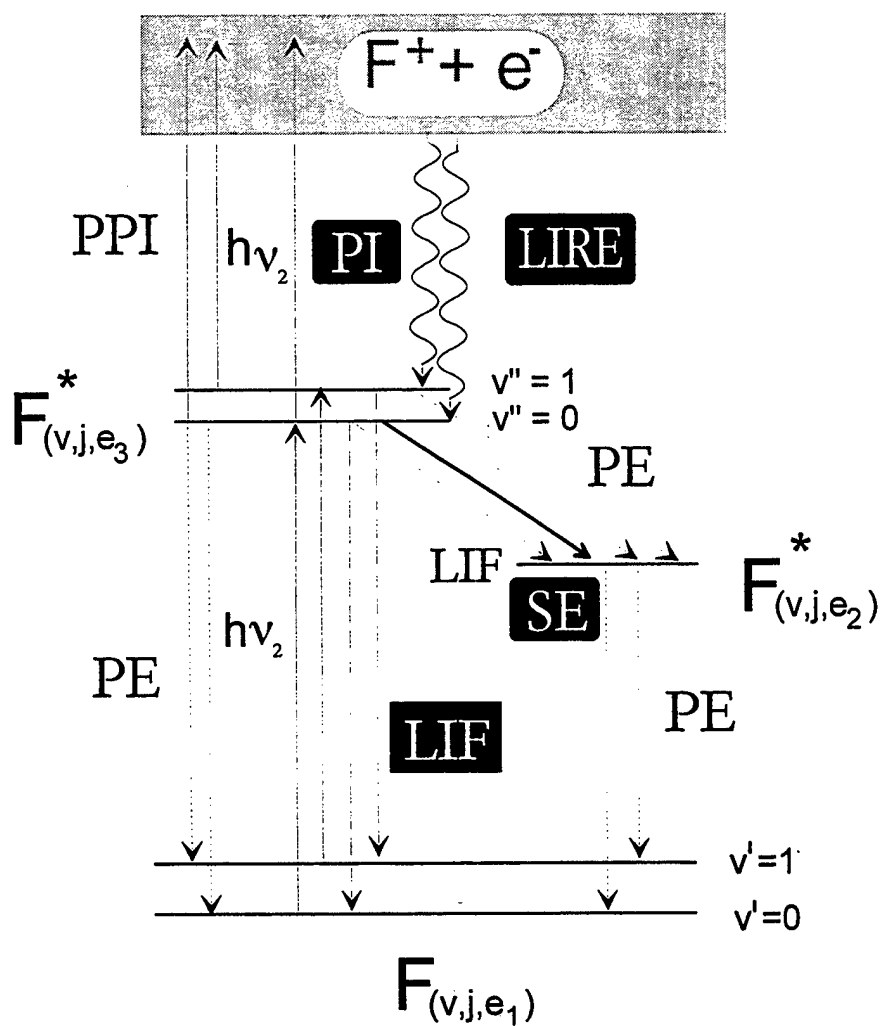


Figure 1. Schematic Diagram Illustrating Several PF/FD Processes, Including LIF, SE, LIRE, PE, PPI, and PI Fragment Detection.

greatest potential in terms of analytical selectivity and sensitivity, as discussed by Antonov and Letokhov [1, 2] and Letokhov [3]. Perhaps the only limitation to PF/PI approaches is the practicality outside the research laboratory.

It is worth noting early reports and reviews, which have been significant in the development of current applications of PF/FD methods. Perhaps the earliest suggestion of PF/FD as an analytical methodology was by Hurst et al. in 1977 [4]. In concluding remarks to their paper, "A Demonstration of One-Atom Detection," the authors identified analytical applications for a resonance ionization spectroscopy approach that included the analysis of "molecular substances, e.g., the classification of a compound by dissociation and subsequent identification of resultant atoms (fragments)."

Since that time, there have been several demonstrations of the feasibility and merits of identifying molecular substances by PF/FD techniques. In 1978, Antonov et al. [5] reported on the detection of several compounds by photoionization and PF/PI techniques, including NO₂, benzaldehyde, benzophenone, nitrobenzene, and *para*- and *ortho*-nitrotoluenes. Antonov and Letokhov [1] later reviewed the use of multiphoton fragmentation and multiphoton ionization techniques for chemical detection. Included in the review was the proposal of a laser selective molecular detector, which incorporated lasers for optical excitation and photoionization of the analyte molecule with mass spectrometric detection. It was concluded that a combination multistep scheme where resonant absorption processes proceeding through vibrational and then electronic intermediate states would be most useful due to the high selectivity that could be achieved.

In 1979, Halpern et al. [6] reported on the study of an ArF laser PF/PE technique used for detecting NH₃ molecules by the emission of NH photofragments. The authors noted the potential for related PF/FD techniques in detecting species such as NO₂ and NO_x, making it the first such suggestion for utilizing PF/FD techniques to monitor atmospheric analytes. Then in 1980, Rodgers et al. [7] published a paper entitled, "Photofragmentation-Laser Induced Fluorescence: A New Method for Detecting Atmospheric Gases," in which PF/LIF was presented as a general strategy for detecting a variety of important atmospheric species. Although no experimental results were

presented, the analytical capabilities were estimated using nominal values for important experimental parameters. Also, they indicated the feasibility of PF/LIF for measuring NO_2 , NO_3 , HNO_2 and laid the foundation for a series of reports on this approach for atmospheric measurements.

Laser multiphoton ionization and fragmentation methods have been reviewed previously by Syage and Wessel [8]. Although the review emphasized PF/FD applications to physical studies, the authors noted an increase in the number of analytical reports and the strong analytical potential of these approaches. Jenkins et al. [9] published a review of PF/FD fluorescence techniques that includes a discussion of the merits of fragment fluorescence spectrometry and a presentation of examples of PF/PE and PF/LIF studies of nonfluorescent species. Important features of the PF/PE and PF/LIF approaches were noted and included the following: (1) their applicability to fluorescent and nonfluorescent molecular analytes; (2) the complementary nature of the information obtained by PF/PE and PF/LIF (regarding neutral fragments), as compared to information by mass spectrometry (regarding ionic fragments); and (3) the "compound class" selectivity obtained by monitoring photofragmented functional groups.

Most recently, Simeonsson and Sausa have reviewed the analytical applications of PF/FD techniques through 1996 [10]. Included in that review are applications of the PF/FD method to the detection of gas phase species by PE, LIF, SE, LIRE, and PI fragment detection. This review is more limited, reporting primarily on applications of the PF/FD method that have appeared since the former review. It is intended to demonstrate the current capabilities of PF/FD techniques and to indicate where future applications are likely to occur in this growing field. For a more comprehensive review of earlier reports, see Simeonsson and Sausa [10].

3. PF/FD Applications Via the Detection of Atomic Fragments

The detection of trace metals in high temperature environments is important both for regulating toxic metal emissions and for controlling emissions of alkali species that are corrosive and result in the degradation of combustion systems. The measurement of these species represents a major area

of application of PF/FD techniques. The analytical utility of the PF/PE approach for detecting gas phase salts of Na and K was initially reported in 1986 by Oldenberg and Baughcum [11], who used an ArF excimer laser (with and without stimulated Raman shifting) as the ultraviolet laser source. Recently, this approach has received renewed attention from several groups. Chadwick et al. [12] have explored the utility of a PF/PE approach for selectively by measuring NaOH in the gas phase in the presence of other Na species. The approach is based on a two photon excited PF/PE where the NaOH molecule absorbs two 355-nm photons from a frequency tripled Nd:YAG laser. This excitation scheme is convenient since it takes advantage of the mature laser technology. Furthermore, the technique selectively produces prompt emission from Na fragments from NaOH, but not those from NaCl. The limit of detection (LOD) for this technique is estimated to be 0.5 parts per million (ppm), and while it is not as sensitive as the use of 193-nm laser radiation, it is selective for NaOH and demonstrates how spectral selectivity of the PF process can be used to distinguish chemical species that contain a common fragment.

Greger et al. [13] have reported on the PF/PE technique for in-situ alkali concentration measurements in a pressurized, fluidized bed reactor. An excimer laser operating at 193 nm photodissociates NaCl and KCl, producing excited $\text{Na}(3^2\text{P})$ and $\text{K}(4^2\text{P})$ atoms whose emissions are simultaneously detected in two separate channels at 589 and 768 nm. Studies on lignite and hard coal under several conditions were performed, and an LOD of <0.2 parts per billion (ppb) was reported for both elements. The dynamic range for the measurements exceeds three orders of magnitude.

Buckley et al. [14] have extended the PF/FD technique to the detection of hazardous metal species in postcombustion gases of a methane/air burner-stabilized flame and reactor [15]. Various metal chloride aerosols were injected in the burner or reactor and exited with 193-nm radiation. Prompt emission from Ba, Cr, Mn, Ni, Pb, and Tl atoms were monitored. LODs in the sub-ppm range have been reported for single- and 100-shot averaging, with negligible spectral interferences between the metal species or background interferences from the combustion products. The highest sensitivity was observed for Tl, with an LOD of 0.5 ppb for 100-shot averaging. The authors reported that the signal changed linearly with concentration for each metal compound injected in the

postflame gases, and in some cases changed with aerosol size and surface area. This latter variation makes the technique a strong function of temperature in the region of the postflame zone where condensation and nucleation are important. The authors show that LODs in the ppb level are readily obtained for the above elements at moderate laser power, despite considerable atmospheric quenching. They indicate that this method is likely to be capable of meeting proposed regulations for metal emissions of combustion devices.

In the PF/PE technique, the major competition for fluorescence is quenching. Depending on the gas composition and temperature, the effective lifetimes for typical metals transitions at atmospheric pressure are one to two orders of magnitude less than their radiative lifetimes. As a result, the fluorescence quantum efficiency Y , $Y = A/(A + Q)$, where A is the spontaneous emission rate and Q is the total quenching rate, is in the range of 1–10% at 1 atm. Hartinger et al. [16] have measured the quenching of fluorescence from Na(3^2P) and K(4^2P) atoms by various collision partners at 973 and 1,273 K following photodissociation of NaCl and KCl at 193 nm. They report quenching cross-sections for CO₂, O₂, and N₂ (10–60 Å²) and Ar (<1 Å²), and calculate an effective fluorescence quantum efficiency for Na (3^2P) in the range of 5–30% at 1 atm using a radiative lifetime of 16 ns and an effective lifetime in the range of 0.8–0.5 ns.

The above works demonstrate that PF/FE is a viable diagnostic for real-time and in-situ monitoring of industrial combustion systems. It is sensitive, nonintrusive, and fast compared to standard sampling methods that require considerably longer measurement times and bear the risk of the sample reacting in the sampling lines. Furthermore, the PF/PE technique is readily implemented due to its simplicity; it only requires a single laser and simple detection optics.

4. PF/FD Applications Via the Detection of Molecular Fragments

PF/FD techniques have been used in a wide range of applications by their characteristic molecular photofragments. Major areas of application have included the measurement of reactive trace gases in the atmosphere, the measurement of halogenated organics in combustion

environments, and the detection of energetic materials (nitrocompounds). For an extensive review of earlier applications, see Simeonsson and Sausa [10].

4.1 NO/NO₂/NO_x. Several groups have reported PF/FD techniques for nitrogen oxides. Peng et al. [17] have explored the utility of two PF-PI schemes for detection of NO_x (NO_x = NO + NO₂). At 226 nm, NO is photoionized by a 1 + 1 process via the A-X (0,0) transition. NO₂ is photolyzed efficiently at this wavelength, and the resulting NO fragments can be detected by the above 1 + 1 PI approach (see Figure 2). The single shot detection limit for NO is reported as 2–3 ppb at 226 nm. The sensitivity for NO₂ is lower and the LOD is estimated to be 10–15 ppb. Alternatively, a 2 + 1 approach at 384 nm can be used to detect NO, for which the LOD is also about 2–3 ppb. Signal averaging is estimated to improve the LOD for the approach to near 0.2 ppb.

Recently, Ledingham et al. [18] explored the use of picosecond (ps) and femtosecond (fs) laser pulses to bypass the dissociative state of NO₂ by fast up-pumping to the NO₂ ion state, thereby increasing the parent ion signal compared to the NO fragment signal. The multiphoton ionization and dissociation of NO₂ is performed at 248 and 496 nm using pulse widths ranging from 15 ns to 300 fs. At 248, the NO₂/NO ion ratio varied from ~1% using 15-ns pulses to about 60% using 300-fs pulses. By comparison, the ion ratios at 496 nm are similar for both 5-ps and 500-fs pulses, but very much reduced from those after photodissociation at 248 nm. The authors interpret their results using a simple rate equation model and conclude that the dissociation rate at 248 nm increases with increasing pulse width for the NO₂ → NO + O(¹D), which opens at 40126 cm⁻¹ (249 nm). More recently, the same group studied the 375-nm multiphoton ionization and dissociation of NO₂ with 10-ns and 50-fs laser pulses [19]. In all spectra, the main peak observed is due to the ionization of the fragment NO, which is formed from the 375-nm dissociation of NO₂. The parent NO₂ ion peak is not observed with nanosecond pulses, but is observed with femtosecond pulses with a NO₂/NO ion ratio of ~10%. These results suggest that selective photoionization of NO and NO₂ species is possible using picosecond and femtosecond laser sources.

Sandholm et al. [20] have reported on the analytical capabilities of PF-LIF techniques for measuring atmospheric NO₂ and NO_y (NO_y = NO + NO₂ + all other sources of NO).

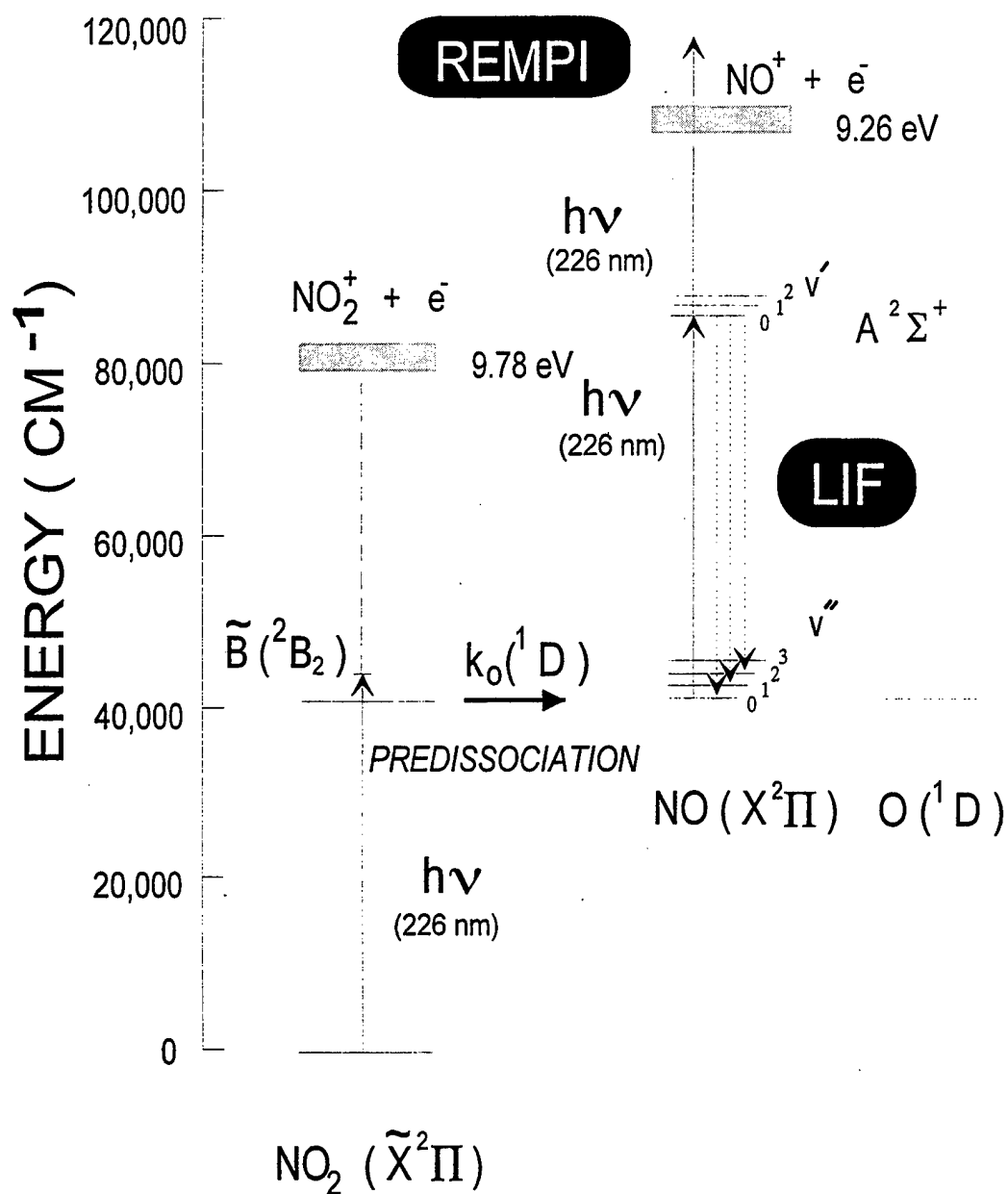


Figure 2. Schematic Diagram Showing the PF/FD Approach for Detecting NO₂ Through NO Fragment Detection Via LIF and REMPI Processes.

The techniques are based on the detection of the NO, which is either photofragmented or produced chemically in a catalytic converter. A recent report describes the latest developments in the detection of NO by LIF, which is based on excitation of NO via the A-X (0,0) transition at 226 nm

and D-A (0,0) near 1,100 nm. This results in fluorescence at the D-X (0,0) transition near 190 nm [20]. Due to the low fluorescence wavelength, the technique is signal limited, resulting in excellent signal-to-noise characteristics and LODs near 1 ppt for NO and other analytes. Instruments based on this detection scheme have been used for aircraft-based measurements of tropospheric NO, NO₂, and NO_y over Alaska, Canada [21, 22], and the Pacific Ocean [23].

Simeonsson and Sausa [24] have reported the trace analysis of NO₂ in the presence of NO by PF/PI at visible wavelengths. NO and NO₂ are differentiated by using laser-visible radiation; NO is detected near 452 nm by (2 + 2) REMPI via its A-X (0,0) transitions, and NO₂ is detected by laser photofragmentation with subsequent fragment NO ionization by means of its A-X (0,0) and (1,1) transitions. Spectral differentiation is possible because the internal energy of the NO photofragment differs from that of “ambient” NO. The LODs for NO and NO₂ are in the 20–40 ppbv range at 449.2, 450.7, and 452.6 nm for a 10-s integration time, and compare favorably with the sensitivity achieved previously for NO₂ at 226 nm. The LOD of NO₂ at 517.5 nm is 75 ppbv.

Simeonsson et al. [25] are exploring techniques for detecting NO by LIF, and NO₂ and NO_x by PF/LIF. Studies using excitation via the A-X (1,0) band near 215 nm, and fluorescence detection via the A-X (0,1) band at 237 nm demonstrate the high sensitivity of this approach. LODs for NO and NO₂ at atmospheric pressure are 0.03 ppb and 5 ppb. Studies are being performed to evaluate the utility of this approach for other nitrogen oxides and the potential for interferences from species such as O₂, O₃, SO₂, and H₂O.

Swayambunathan and Sausa [26] have explored the use of a two-color PF/FD scheme for detecting NO₂. An Nd:YAG laser operating at 355 nm was used to both excite NO₂ and to pump a dye laser whose output is frequency doubled to produce 226-nm radiation. The NO fragment is detected by LIF using its A-X (0,0) transitions. It was found that the sensitivity approximately doubled from 200 to 100 ppb when using both 355- and 226-nm radiation, compared to using only 226-nm radiation. The increase in sensitivity is attributed to the generation of more NO from the dissociation of NO₂ at 355 nm.

4.2 NH₃. The detection of atmospheric NH₃ is an important application of PF/LIF. Studies by Schendel et al. [27] and Williams et al. [28] at Georgia Tech have shown in the laboratory and in the field that a PF/LIF approach based on the PF of NH₃ at 193 nm with subsequent LIF of the NH photofragments (excitation at 450 nm, detection at 325 nm) is highly effective for measurements in the open atmosphere [27, 28]. The spectral selectivity of this technique is such that isotopic tracer studies can be performed using a radio labeled ¹⁵NH₃. Intercomparison studies have also demonstrated the superiority of the PF/LIF approach over any other method in terms of accuracy, precision, and response time [28]. A version of this instrument was flown as part of the NSF-ACE I program, although the results have not been published [29].

4.3 H₂SO₄, SO₂. Sulfur compounds play a critical role in atmospheric chemistry and the measurement of sulfur species by PF techniques has been reported. Omenetto et al. [30] and Omenetto and Panne [31] have reported on a PF/PE technique for the detection of H₂SO₄ aerosol droplets and SO₂ using an ArF excimer laser operating at 193 nm. While irradiation of the H₂SO₄ aerosols produced broad band emission spectra, irradiation of SO₂ resulted in SO₂ emissions that were superimposed with emissions attributed to SO photofragments. The SO emissions are believed to result from SO photofragments that are subsequently excited by ArF laser radiation. An alternative PF/PD approach for measuring H₂SO₄ droplets based on their reaction with NaOH and emission-volatilized Na atoms is also being explored [32].

4.4 HO₂. The hydroperoxyl radical (HO₂) is important in both atmospheric and low temperature combustion environments. Hynes et al. [33] have developed a two-color PF/LIF technique for detecting HO₂. HO₂ is photolyzed at 212 nm by the fifth harmonic output of an Nd:YAG laser, generating the O and OH fragments. The OH is then detected by LIF by means of its A-X (1,0) band near 282 nm. The OH LIF signal is directly proportional to the HO₂ concentration because both the photolysis and probe pulses are generated simultaneously or slightly delayed by the same laser system. A detection limit of $2 \times 10^{11} \text{ cm}^{-3}$ has been reported in 300 Torr of N₂, indicating that the approach has the sensitivity and temporal resolution to be useful for kinetic studies of HO₂ under atmospheric conditions.

4.5 Nitrocompounds Including Energetic Materials. Various nitro-containing organic compounds, including energetic materials, have been measured using PF/FD. The multiphoton ionization and dissociation of nitromethane using nanosecond and femtosecond laser pulses at 375 and 750 nm was investigated by Kilic et al. [34]. The nanosecond time-of-flight spectra revealed only one peak at $m/e = 30$, corresponding to the NO photofragment. But the femtosecond spectra revealed a number of peaks, the prominent ones attributable to the parent ion, NO_2 , NO, and CH_3 . The spectra recorded using 90 fs of 750-nm radiation were similar to those recorded using 90-fs of 375-nm radiation, but with the parent peak considerably reduced.

Recently, the same group extended their nanosecond and picosecond laser studies to the ionization and photodissociation of nitrobenzene and o-, m-, and p-nitrotoluene isomers at 375 nm [35]. As in the nitromethane studies, these studies show that the parent molecule can be ionized with 90 fs pulses with great efficiency by bypassing its dissociative, molecular-excited states. This enhances the analytical utility for nitrocompound detection by minimizing parent photofragmentation and increasing parent ionization. Furthermore, the mass spectra of the nitrotoluene isomers show significant differences, enhancing their selectivity.

Wu et al. [36] report the detection of TNT by PF/LIF as part of an effort to develop a laser-based optical sensor for monitoring soil contaminated with energetic materials. A 226-nm laser is used to both photofragment the target compound and detect the characteristic NO fragment by LIF via its A-X (0,0) transitions. The concentration of the target compound is inferred from the intensity of the NO fluorescence. The effects of temperature and pressure on the PF/LIF signal were studied, and it was found that the signal significantly increased when the sample was heated above 343 K. Physical and chemical changes of the sample were noted at these temperatures. A detection limit of 4 ppm is reported for TNT in soil, showing that the PF/LIF holds great promise as a detection technique for energetic materials in soil.

Recently, Swayambunathan and Sausa [26] applied the PF/FD technique for the detection of RDX, PETN, and TNT. The technique employed a single laser operating at 226 nm and low pulse energies (100 μJ) for both photofragmenting the parent molecule and detecting the NO fragment by

REMPI or LIF. The REMPI technique appears to be more useful for ambient studies because the ion signal can be measured without heating the sample to high temperatures where decomposition can occur, as observed in the case of RDX and PETN. The REMPI LODs ($S/N=3$) are 70 ppm for TNT, 2 ppm for PETN, and 7 ppm for RDX.

5. Future Outlook for PF/FD Applications

As the above reports indicate, the majority of applications of PF/FD techniques have been in two areas: (1) the measurement of trace atmospheric species, especially nitrogen oxides and NH_3 ; and (2) the measurement of volatile alkali and heavy metal compounds in combustion exhaust gases. Other important areas of application include the measurement of chlorinated compounds in combustion exhaust gases and the development of PF/LIF and PF/PI approaches for measuring nitrocompounds (R-NO_2) with the goal of detecting energetic materials through in situ detection of their vapors. A summary of the PF/FD reports described in this review is given in Tables 1 and 2. A common theme for these efforts is the strong need for analytical approaches that allow in situ measurements and provide high sensitivity and selectivity on a real-time or near real-time basis. As more analytical chemistry measurements are pursued in situ, there will be even greater motivation for developing laser-based PF/FD approaches.

PF/FD sensors have already been demonstrated for measurements of $\text{NO}_2/\text{NO}_x/\text{NO}_y$, HNO_3 , HONO, and NH_3 , and it is expected that these techniques will continue to be developed and utilized for these same species. It is also expected that PF/FD approaches will be extended to other atmospheric species such as CH_3I , OI , CH_3Br , and dimethylsulfide (DMS). Furthermore, it is anticipated that PF/FD approaches will be useful for monitoring metal containing species and halogenated species in combustion environments and will continue to be explored for the detection of energetic materials and explosives. Continued advances in solid-state laser technology, combined with the fact that PF/FD approaches can be carried out remotely through optical fibers, indicates a strong potential for sensing and monitoring applications, especially in difficult or hostile environments. The high sensitivity and selectivity of PF/FD approaches is certain to lead to future growth in the number of applications of these powerful analytical techniques.

Table 1. PF/FD Chemical Analysis by Atomic Fragment Detection

F	R-F	Method	$\lambda_{[PF]}$ (nm)	$\lambda_{[FD]}$ (nm)	Transition	LOD (ppb)	Ref.
Na	NaOH	PF/PE	193	589	$3p^2P^o - 3s^2S$	500	[12]
Na	NaCl	PF/PE	193	589	$3p^2P^o - 3s^2S$	<0.2	[13]
K	KCl	PF/PE	193	768	$4p^2P^o - 4s^2S$	<0.2	[13]
Ba	BaCl ₂	PF/PE	193	455.4 493.4 553.6	$6p^1^2P_{3/2} - 6s^1^2S_{1/2}$ $6p^1^2P_{1/2} - 6s^1^2S_{1/2}$ $6p^1^1P_1 - 6s^1^1S_0$	30	[14, 15]
Cr	CrCl ₂	PF/PE	193	357.8	NI	300	[14, 15]
Mn	MnCl ₂	PF/PE	193	403.0	$3d^5 4s^1 4p^1 z^6P - 3d^5 4s^2 a^6S$	200	[14, 15]
Ni	NiCl ₂	PF/PE	193	300.3	NI	150	[14, 15]
Pb	PbCl ₂	PF/PE	193	405.8	$^3P^o_1 - ^3P_2$	15	[14, 15]
Tl	TlCl ₃	PF/PE	193	377.5	$^2S_{1/2} - ^2P^o_{1/2}$	1.5	[14, 15]

Table 2. PF/FD Chemical Analysis by Molecular Fragment Detection

F	R-F	Method	$\lambda_{[PF]}$ (nm)	$\lambda_{[FD]}$ (nm)	Transition	$\lambda_{[FL]}$ (nm)	LOD	Ref.
NO	NO ₂	PF/REMPI	226 450.7 452.6 517.5 226	226 450.7 452.6 517.5 226	A-X(0,0) A-X(0,0) A-X(0,0) A-X(0,3) A-X(0,0)		10–15 ppb 25 ppb 15 ppb 75 ppb 22 ppb	[17] [24] [24] [24] [37]
NO	NO ₂	PF/LIF	350–420 215	226/1100 215	A-X(0,0)/D-A(0,0) A-X(1,0)	190 237	6 ppt 5 ppb	[22] [25]
NH	NH ₃	PF/LIF	193	450	A-X	325	4–10 ppt	[27]
SO	SO ₂ H ₂ SO ₄	PF/PE	193	913	NI		NI	[30–32]
OH	OH ₂	PF/LIF	212	212	A-X(1,0)	308	$2 \times 10^{11} \text{ cm}^{-3}$	[33]
NO	TNT	PF/PI	226	226	A-X(0,0)		70 ppb	[26]
	RDX	PF/PI	226	226	A-X(0,0)		7 ppb	[26]
	PETN	PF/PI	226	226	A-X(0,0)		2 ppb	[26]
NO	TNT	PF/LIF	226	226	A-X(0,0)	226–260	37 ppb	[26]

Note: NI = not indicated.

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Glossary

FD	Fragment detection
LIF	Laser-induced fluorescence
LIRE	Laser ionization recombination emission
LOD	Limit of detection (3 s unless specified otherwise)
MS	Mass spectrometry
PE	Prompt emission
PF	Photofragmentation
PIS	Photoionization spectrometry
REMPI	Resonance-enhanced multiphoton ionization
SE	Stimulated emission
TPI	Two photon ionization

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